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Soil Organic Matter Characteristics as Affected by Tillage Management

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ABSTRACT

Soil organic matter (SOM) is of primary importance for maintaining soil productivity, and agricultural management practices may significantly influence SOM chemical properties. However, how SOM chemical characteristics change with agricultural practices is poorly understood. Therefore, in this study, we evaluated the impacts of tillage (conventional vs. conservation) management on the structural and compositional characteristics of SOM using cross-polarization magic-angle-spinning (CPMAS) and total sideband suppression (TOSS) solid-state ^{13}C nuclear magnetic resonance (NMR) and diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy. We characterized both physically and chemically isolated SOM fractions from a Norfolk soil (fine-loamy, siliceous, thermic Typic Kandiudults) under long-term tillage management (20 yr). The solid-state ^{13}C NMR results indicated that humic acid (HA) from conventional tillage (CT, 0–5 cm) was less aliphatic and more aromatic than HA from conservation tillage (CnT). The aliphatic C content decreased with increasing depth (0–15 cm) for both CT and CnT treatments. The reverse trend was true for aromatic C content. Based on reactive/recalcitrant (O/R) peak ratio comparisons, HA was more reactive in the top soil (0–5 cm) under CnT than CT. Both soil organic C (SOC) and light fraction (LF) material were higher in the 0- to 5-cm soil of CnT than CT treatment. Our results show that long-term tillage management can significantly change the characteristics of both physical and chemical fractions of SOM.

S OIL ORGANIC MATTER strongly affects soil properties such as water infiltration rate, erodibility, water holding capacity, nutrient cycling, and pesticide adsorption (Stevenson, 1994; Campbell et al., 1996; Francioso et al., 2000; Wander and Yang, 2000). It has been suggested that proper management of SOM is the heart of sustainable agriculture (Weil, 1992). Recent research has also recognized SOM as a central indicator of soil quality and health (Soil and Water Conservation Society, 1995). For example, a decline in SOM (biological oxidation or erosion) significantly reduced the N supply and resulted in a deterioration of soil physical conditions, leading to crop yield reduction (Greer et al., 1996). Therefore, it is important to maintain proper levels of SOM to sustain soil productivity.

Intensive agricultural practices change SOM characteristics greatly, generally a substantial loss of soil organic C (SOC). Soils of the southeastern United States of America, particularly sandy Coastal Plain soils, have inherently low SOC contents (typically below 1%, Hunt et al., 1982). Consequently, small changes in the SOM content are significant to the agricultural production of the region. An evaluation of tillage and crop residue management practices to rebuild SOC levels has been conducted by Hunt et al. (1996). These researchers monitored changes in SOC levels in numerous small tillage plots and found that after 9 yr of CnT, the SOC content in the top few centimeters was significantly higher than the soil under CT management. Campbell et al. (1999) reported that over an 11- to 12-yr period, increases in C storage in the 0- to 15-cm soil depth, because of adoption of no-tillage, were small (0–3 Mg ha^{-1}). Most of the differences were observed in the 0- to 7.5-cm soil depth, with little change in the 7.5 to 15 cm. However, the short and long-term influences of disturbance on C mineralization are complex and may vary depending on types of soil and plant residues (Hu et al., 1995; Franzleubbers and Arshad, 1996; Alvarez et al., 1998). The strong influence of soil management on the amount and quality of SOM was also reported by others (Janzen et al., 1992; Ismail et al., 1994; Campbell et al., 1996).

Another approach to evaluate the impact of agricultural management on SOM dynamics is to separate SOM into pools based on differences in decomposition rates (Wander et al., 1994; Wander and Traina, 1996a). Generally, those pools are conceptualized with one small pool having a relatively quick decomposition rate (i.e., active pool LF) and pools that are more recalcitrant (i.e., humus) (Stevenson, 1994). The LF is sensitive to environmental and agricultural management factors and can be used as a functional description of organic materials (Wander and Traina, 1996a). Regardless of active or recalcitrant SOM pools, structural chemistry is important for their chemical and biological activities.

Spectroscopic techniques can provide useful structural information of SOM. Diffuse reflectance Fourier transform infrared spectroscopy is considered to be one of the most sensitive infrared techniques for humic substances analysis (Niemeyer et al., 1992; Ding et al., 2000). According to Painter et al. (1985) and Niemeyer et al.

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(1992), this technique offers several advantages over transmission infrared spectroscopy: (i) a simple sample-preparation procedure; (ii) insensitivity to water associated with the sample and enhanced resolution; (iii) high resolution of the spectra because of reduction in the sensitivity towards light scattering; and (iv) a more reliable method for quantitative estimations of functional groups. Another spectroscopic technique is solid-state ^{13}C NMR spectroscopy that is probably the most useful tool for nondestructive characterization of SOM and its components (Preston, 1996; Xing and Chen, 1999; Mao et al., 2000). Studies by Capriel (1997) and Ding et al. (2000) demonstrate that both DRIFT and ^{13}C NMR techniques are useful and suitable for examining the effects of agricultural management on SOM.

The goal of this research was to evaluate the changes of SOM quantity and quality under CT and CnT systems using both DRIFT and solid-state ^{13}C NMR. Spectroscopic investigations of SOM changes for the Norfolk soil, located in the Southeastern Coastal Plain, have never been conducted before. Furthermore, because organic, sustainable agricultural systems depend increasingly on soil nutrient cycling mechanisms, it is necessary to understand the relationships between the LF, the structural and compositional changes of HA, and nutrient retention and supply characteristics. The specific objectives were to: (i) characterize HA structural changes; (ii) determine peak height O/R ratio for HA, which reflects the biological activity; and (iii) compare the light fraction (LF) variations with soil depth under both CnT and CT systems.

MATERIALS AND METHODS

Site Description and Sampling

The study was conducted using soil samples collected from the long-term CnT and CT research plots established in 1979 at the Clemson University Pee Dee Research and Education Center (Darlington, SC). The soil at the research site is a Norfolk loamy sand. The coordinates are 34.3° N lat. and 79.7° W long., and the elevation is 37 m above the mean sea level. Treatments were arrayed in a randomized complete block design with split plots and five replications (Hunt et al., 1996).

The CT treatment within the plots consisted of multiple disking (0–15 cm deep) and the use of field cultivators to maintain a relatively weed free surface. Surface disking and field cultivation have been completely eliminated in soil under CnT plots since 1979. Because of a root-restrictive E horizon which reforms annually in this soil (Busscher and Sojka, 1987), both tillage treatments received in-row subsoiling (30 cm deep) at planting to fracture this horizon. Additional management practices for the plots such as crop rotation, fertilization, and pesticide application were described previously (Hunt et al., 1996; Novak et al., 1996). In 1999, ~50 soil cores were collected from the top 15 cm of soil using a 2.5-cm diam. soil probe at random locations from one plot under CnT and one plot under CT treatment. The core samples were sectioned (5-cm increments), composited, air-dried, and sieved (2 mm).

Density Gradient Separation of Light Fraction Material and Analysis

The LF has been recognized to be an important soil nutrient reservoir and has been recommended as a fertility index (Wander et al., 1994). In this investigation, the LF material from

each soil layer was isolated using a modified density gradient method of Wander and Traina (1996a). The LF was collected by dispersion of 50 g soil of freshly sieved, field-moist soil sample in a NaBr solution (density 1.5 g mL^{-1}, 1:1 w/v). The mixture was shaken for 30 min and centrifuged at 7500 × g (8000 rpm) for 20 min. These rinses were then transferred into a 250-ml separatory funnel and allowed to settle overnight. After three such separations, the composite supernatant was filtered using a 0.45-μm polycarbonate membrane filter. The heavy SOM fraction which settled to the bottom of the funnel was removed. The LF materials retained on the filter were rinsed with a 0.5 M CaCl$_2$ and 0.5 M MgCl$_2$ solution followed by a final rinse in deionized water. This was done to avoid any remnant biological toxicity because of Na$^+$ saturation of the ion-exchange sites in the LF. The weight yield of LF was measured and the light fraction organic C (LF-OC) and total combustible N content were determined using a LECO-CN 2000 analyzer (LECO Corp., Joseph, MI).

Extraction, Fractionation, and Purification of HA and Elemental Composition Analysis

Most of extraction techniques require the organic matter to be removed from soil (Stevenson, 1994). As a consequence, the OC constituents would be modified to some extent. Therefore, we used neutral pyrophosphate (Na$_4$P$_2$O$_7$) to extract SOM to minimize chemical modifications (Stevenson, 1994). Air-dry and sieved soil (50 g) was weighed into a 1000-ml plastic bottle, and 500 ml of 0.1 M Na$_4$P$_2$O$_7$ were added. The air in the bottle and solution was displaced by N gas (N$_2$) and the system was shaken for 24 h at room temperature. The samples were extracted three times. After separation from the Na$_4$P$_2$O$_7$ insoluble residues by centrifuging at 1100 × g (3000 rpm), the dark-colored supernatant solutions were combined, acidified to pH 1 with 6 M HCl, and allowed to stand for 24 h at room temperature for the precipitation of the HA fraction. The HA was shaken for 24 h at room temperature with 0.1 M HCl/0.3 M HF solution at least for three times. The insoluble residues (HA) was separated from the supernatant by centrifuging at 12 000 × g (10 000 rpm), washed with deionized water until free of Cl$^-$ ions, and then freeze-dried. The C, H, and N contents of the isolated HAs were measured with a Fisons Model EA 1108 Elemental Analyzer (Mattson Instrument, Madison, WI).

Diffuse Reflectance Fourier Transform Infrared Analysis

The DRIFT spectra were collected using an Infrared Spectrophotometer (Midac series M 2010, Midac Corp., Irvine, CA) with a DRIFT accessory (Spectros Instruments, Shrewbury, MA). All HA fractions were powdered with an agate and pestle and stored over P$_2$O$_5$ in a drying box. Three-milligram solid HA samples were then mixed with KBr (total weight as to 100 mg) and reground to powder consistency. A sample holder was filled with the mixture (powder). A microscope glass slide was used to smooth the sample surface. At the beginning of analysis, the diffuse-reflectance cell which contained the samples was flushed with N$_2$ for 10 min to reduce the interference from CO$_2$-C and water molecules. The sample compartment was placed with anhydrous Mg(ClO$_4$)$_2$ to further reduce atmospheric moisture.

The DRIFT spectroscopy was acquired with a minimum of 100 scans collected at a resolution of 16 cm^{-1}. The spectroscopy was calibrated with the background which consisted of powdered KBr and scanned under the same environmental conditions as the sample-KBr mixtures. Absorption spectra were converted to a Kubelka-Munk function using Grams/32 software package (Galactic Corp., Salem, NH). Peak assignments

and intensity (by height) ratio calculation were done following the methods of Niemeyer et al. (1992), and Wander and Traina (1996b). We used ratios of labile (O-containing) and recalcitrant (C and H or N) functional groups to compare HA spectra with varying soil depth of different tillage treatments.

Solid-State Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Spectra were obtained by using the CPMAS-TOSS techniques. Xing et al. (1999), after examining several solid-state ^{13}C NMR techniques including ramped CPMAS, reported that CPMAS-TOSS has two advantages. The first is that an adequate TOSS can eliminate the sidebands so that the spectrum shows only the true peaks for a given HA sample. The second is that implementation of cross-polarization-TOSS can avoid baseline distortion from the dead time. In addition, instrument time required is about the same as the regular CPMAS. They recommended that CPMAS-TOSS be used to analyze HA samples when using a ≥300 MHz spectrometer. In this research, HA samples were run at 75 MHz (^{13}C) in a Bruker MSL-300 spectrometer (Bruker, Billerica, MA) with a 7-mm CPMAS probe. The samples (300–350 mg) were packed in a 7-mm-diam. zirconia rotor with a Kel-F cap. The spinning speed was 4.5 kHz. A ^{1}H 90° pulse was followed by a contact time (t_{cp}) of 500 μs, and then a TOSS sequence was used to remove sidebands (Schmidt-Rohr and Spiess, 1994; Xing et al., 1999). Line broadening of 30 Hz was used. The 90°-pulse length was 3.4 μs and the 180° pulse was 6.4 μs. The recycle delay was 1 s with the number of scans ~4096. The details were reported elsewhere (Xing et al., 1999). In preliminary experiments, we ran several samples at different contact times, and selected 500 μs because this contact time gave the best signal/noise ratio and the spectra were similar to the ones generated by direct polarization magic-angle-spinning ^{13}C NMR. There was no signal observed for the rotor and Kel-F cap (Mao et al., 2000), thus, no background correction was made in this work.

Statistical Analyses

All data presented were the mean of at least three replicate measurements, except for HA elemental composition and solid-state ^{13}C NMR data because of the high cost and low availability of the instrument. However, preliminary solid-state NMR experiment with one HA sample indicated minimal variations, which was consistent with the result of an extensive NMR study in our lab (Mao et al., 2000). The HA elemental composition and NMR measurements were performed on composite samples.

The fraction of total SOC and total combustible N (TCN) pools in the unfractionated soil and in LF was compared using a two-way Analyses of Variance (ANOVA). Also, the O/R ratios generated from DRIFT peak heights were examined between tillages and by depth using the ANOVA. Different tillage treatments and soil depths were the experimental factors and the interactions between tillage and depth were examined. SigmaStat software (SPSS Corp., Richmond, CA) was used for each test at a 0.05 level of significance.

RESULTS

Yields of Light Fraction Material and Elemental Composition of Humic Acid

The total quantities of SOC, TCN, and LF found in soils calculated from bulk density under CnT and CT

Table 1. Soil organic C (SOC), total combustible N (TCN), and light fraction (LF) in the soil under different tillage systems (standard deviation in parentheses).†

	Soil depth	CnT	CT
	cm	kg m^{-2}	
SOC	0–5	2.30 (0.02)a‡	1.22 (0.01)a
	5–10	0.89 (0.01)b	1.23 (0.01)a
	10–15	0.61 (0.01)b	0.81 (0.01)b
TCN	0–5	0.22 (0.01)a	0.11 (0.00)a
	5–10	0.08 (0.01)b	0.11 (0.00)a
	10–15	0.05 (0.00)b	0.06 (0.00)b
LF	0–5	1.19 (0.02)a	0.63 (0.01)a
	5–10	0.17 (0.01)b	0.55 (0.01)a
	10–15	0.10 (0.00)b	0.12 (0.00)b
		C/N ratio of Soil	
C/N	0–5	10.4 (0.02)a	11.1 (0.01)a
	5–10	11.1 (0.02)a	11.2 (0.01)a
	10–15	12.2 (0.02)a	13.5 (0.03)a
		g kg^{-1}	
LF-OC/SOC	0–5	160 (4.01)a	150 (3.48)a
	5–10	40 (1.55)b	130 (2.78)a
	10–15	42 (1.78)b	42 (1.29)b
LF-N/TCN	0–5	100 (2.45)a	90 (2.07)a
	5–10	30 (1.38)b	80 (2.17)a
	10–15	22 (1.29)b	22 (1.69)b

† Aerial mass of SOC, TCN, and LF was calculated from area and soil bulk density.
‡ Means with different letters are significantly different P = 0.05.

management are shown in Table 1. It is clear that 20-yr different tillage management influenced the quantity and distribution of C, LF, and N in the soil. Twenty-year CnT treatment resulted in a significant increase in the SOC, soil-TCN, and LF in the top 0- to 5-cm soil layer of the unfractionated soil, as compared with CT management. The quantities of SOC, TCN, and LF in the 0- to 10-cm layer were significantly higher than those of 10- to 15-cm depth under CT treatment. The SOC and TCN decreased with increasing soil depth under both tillage treatments.

The quantity of LF material in the 0- to 5-cm soil layer in the CnT system was approximately twice high as that in the CT system. On the other hand, soil under CT management at the 5- to 10-cm layer had significantly higher LF than soil under CnT. The dependency of tillage and depth on LF distribution was confirmed by the two-way ANOVA which showed that there was a significant tillage and depth interaction ($P < 0.01$) when the quantity of LF was compared between tillages. Additionally, regression analyses between the quantity of LF material and the quantity of SOC showed a significant linear relationship (r^2 between 0.89 and 0.97, $P ≤$ 0.01) (data not shown). This relationship indicates that 89 to 97% of the variation in quantity of LF material isolated from soil under both tillages can be accounted for by the SOC content.

The isolated LF material accounted for between 4 and 16% of the total SOC and 2 to 10% of soil TCN from the Norfolk soil (Table 1). Only at the 5- to 10-cm soil depth was there a significant difference of LF-OC and LF-N percentages between tillages. Regression analyses confirmed a significant relationship (r^2 between 0.79 to 0.95) between the LF-OC vs. the SOC content and the LF-TCN vs. the soil-TCN content. The

Table 2. Elemental composition of humic acids on an ash-free basis and atomic H/C and C/N ratios.

Sample	Depth	C	H	N	H/C	C/N
	cm		g kg^{-1}			
CnT	0–5	527	41	39	0.94	15.7
CnT	5–10	479	36	31	0.92	18.1
CnT	10–15	516	35	31	0.81	19.4
CT	0–5	546	40	37	0.88	17.2
CT	5–10	548	40	35	0.88	18.3
CT	10–15	538	40	31	0.89	20.3

soil C/N ratio for both tillages increased slightly with soil depth, but not significantly (Table 1).

The elemental compositions of the HAs from both CnT and CT systems are displayed in Table 2. Examination of the data showed that the HAs from two tillage systems were similar to each other. The C content of HA under CnT was slightly lower in the middle layer (5–10 cm) than that of other two layers. The N content was higher in the top soil than that of deeper layers for both tillages. The HA atomic C/N ratio increased with soil depth for both tillages, similar to the soil C/N ratio changes. The HA H/C ratio of CnT plot slightly declined with depth while this ratio was almost constant for CT soil.

Solid-State Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Humic Acid

The HA ^{13}C CPMAS-TOSS NMR spectra of both CT and CnT are shown in Fig. 1. The HA spectra revealed generic chemical characteristics of the components present in the samples. Unsubstituted aliphatic C is indicated by signals in the 0- to 50-ppm region. Carbons in proteinaceous materials (amino acids, peptides, and proteins) have resonances between 40 and 60 ppm, and C in carbohydrates gives signals between 60 to 108 ppm. Signals between 108 to 162 ppm are because of aromatic C, while those near 155 ppm arise from phenolic C, indicating the presence of O- and N-substituted aromatic groups (e.g., phenolic OH and aromatic NH$_2$). The strong signals between 170 and 180 ppm come from C in carboxyl groups, with possibly some overlapping from phenolic, amide, and ester carbons (Stevenson, 1994; Mao et al., 2000).

It was difficult to directly compare the HA spectra of different treatments because visual comparison showed no major differences in terms of presence or absence of specific peaks. However, we can obtain detailed information from these spectra by peak area integration. The relative content of major C-types, calculated by integrating the spectral profile according to standard chemical shift ranges (Xing et al., 1999) is shown in Fig. 2. The most noticeable feature was at 60 to 96 ppm region (Fig. 1 and Fig. 2B), i.e., carbohydrate-C (aliphatic C bonded to OH groups, ether oxygens, or occurring in saturated five or six-membered rings bonded to oxygens). This C content for CnT in the top soil (0–5 cm) was 23.9%, and was 18.3% for CT (Fig. 3B). The difference between the two treatments can be attributed
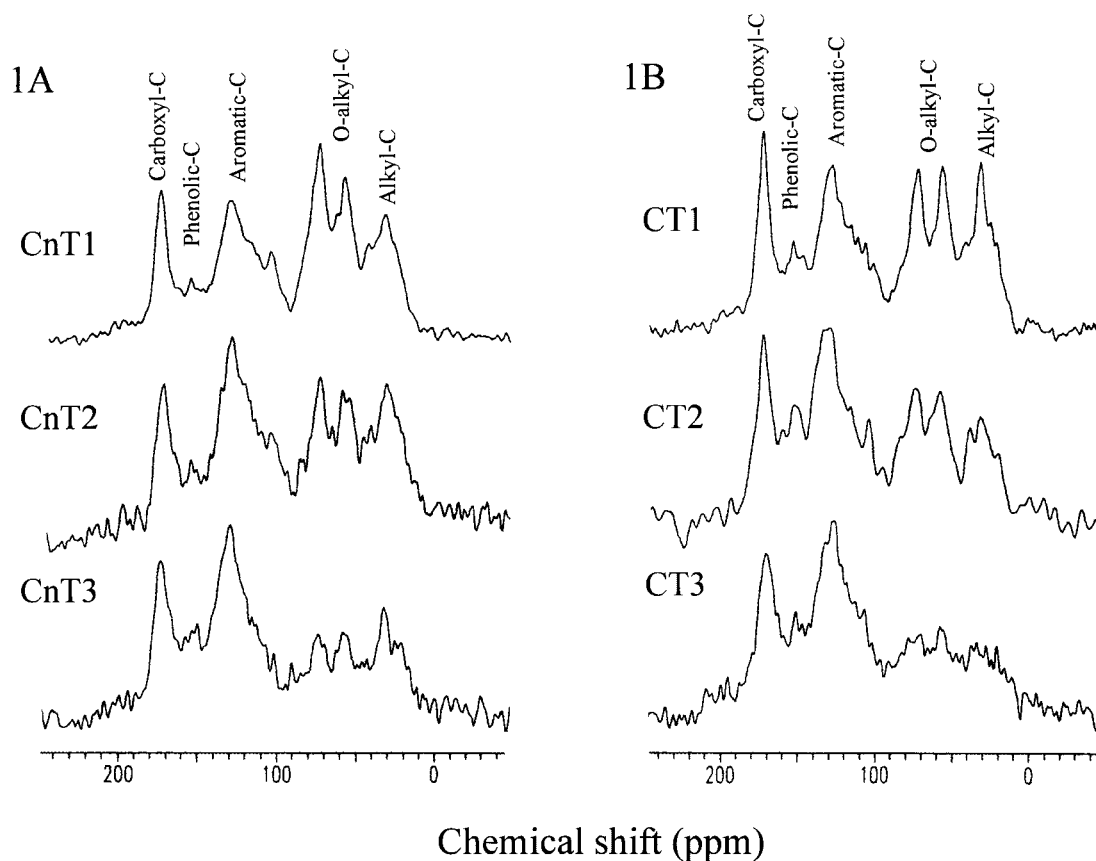
Fig. 1. Cross-polarization magic angle-spinning total sideband suppression ^{13}C NMR spectra of humic acids in a Norfolk soil under different tillages: (1A) conservation tillage treatment (CnT1, 0–5 cm; CnT2, 5–10 cm; and CnT3, 10–15 cm); (1B) conventional tillage treatment (CT1, 0–5 cm; CT2, 5–10 cm; and CT3, 10–15 cm).

to the accumulation of carbohydrate materials from fresh residue input in the top soil of CnT treatment. The reverse trend was true in the 10- to 15-cm layer, which showed carbohydrate-C content was higher in CT than that of CnT system. There was not much difference in the 5- to 10-cm layer between both tillages. The lowest carbohydrate-C for both tillage managements occurred at 10- to 15-cm soil layer. The carbohydrate-C decreased with soil depth for CnT. But for CT management, the carbohydrate-C content was almost the same in the first two layers.

The total aliphatic C (0–108 ppm) of HA for CT treatment (Fig. 2A) decreased from 52.5% in the top soil (0–5 cm) to 40.1% at the depth of 10 to 15 cm. Similarly, the aliphatic C of HA for CnT treatment decreased from 58.8% in the top soil (0–5 cm) to 40.8% at the depth of 10 to 15 cm. Furthermore, when comparing the total aliphatic-C (0–108 ppm) and carbohydrate-C (60–96 ppm) of HA between the two treatments (Fig. 2A and 2B), it was evident that both aliphatic-C and carbohydrate-C were higher in the top (0–5 cm) soil of CnT than CT. The HA alkyl-C content (0–50 ppm, data not shown) at the 10- to 15-cm layer was higher in CnT than CT.

Another interesting feature was revealed by the 108 to 162 ppm of NMR spectra and their integration results (Fig. 1A,B, and Fig. 2C). The two most pronounced peaks in this region were recorded at ~131 ppm (ring carbons in which the ring is not substituted by strong electron donors such as O and N) and at 155 ppm (phenols and aromatic amines). Aromatic-C (31.7%) in the 0- to 5-cm layer under CT was higher than that (28.1%) of CnT treatment (Fig. 2C). Similarly, HA aromatic-C content in 5 to 10 cm of CT system was greater than that of CnT plot. However, the aromatic-C content was almost the same in the 10 to 15 cm for both tillages, even though aromatic-C in both treatments increased with soil depth. The aromaticity (expressed in terms of aromatic-C as a percentage of the aliphatic-C + aromatic-C, according to Hatcher et al., 1981) increased from 32.3% in the top soil of CnT to 50.7% at the 10- to 15-cm layer, and from 31.7 to 50.8% for CT treatment (Fig. 2D). Carboxyl groups were relatively enriched in CT treatment (data not shown). The value of carboxyl-C increased with soil depth for both treatments, which was consistent with the report by Stearman et al. (1989). The chemical shift of carbonyl-C was distinct only for a few HA samples (e.g., CnT2 and CT3)
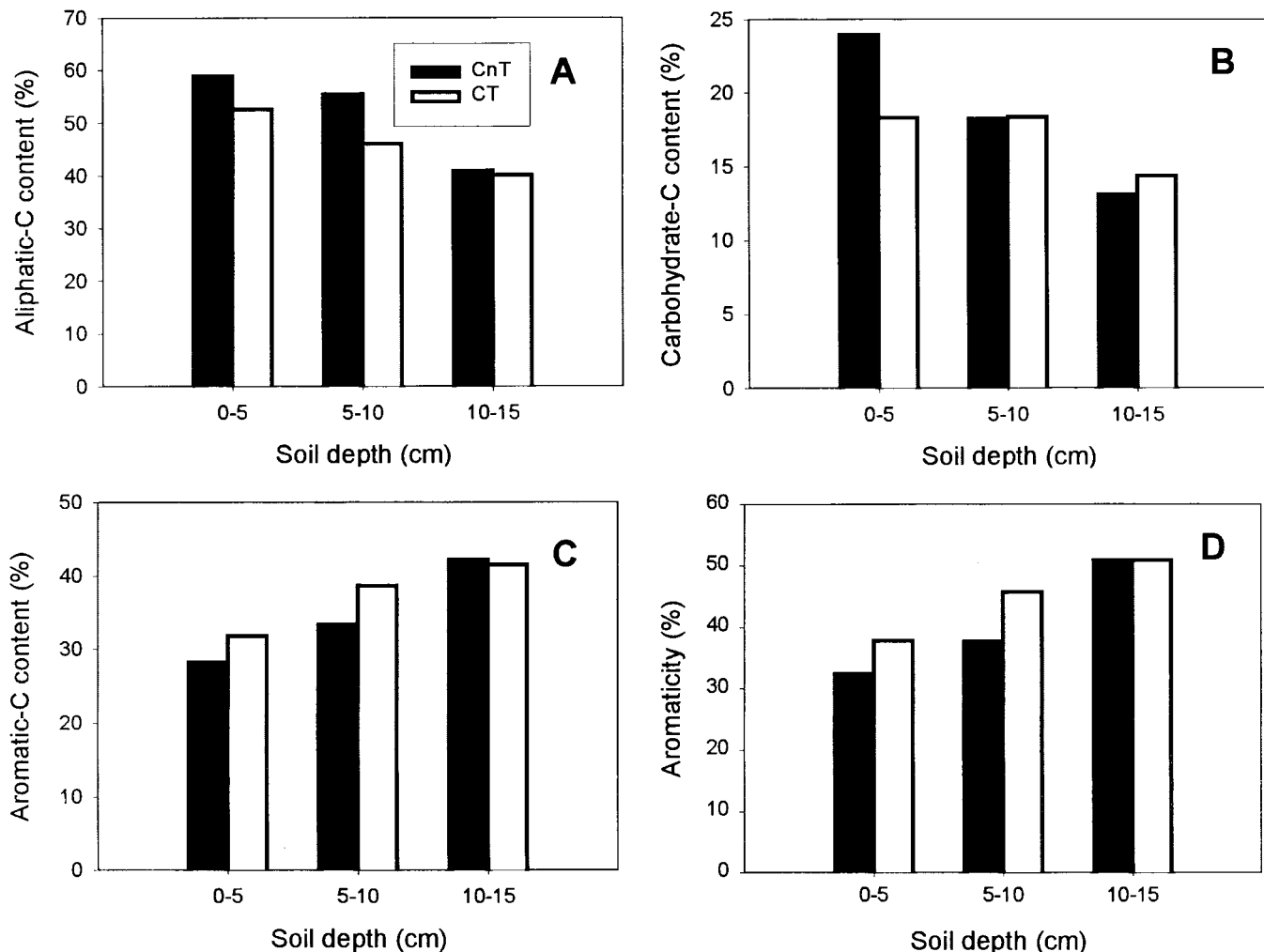

Fig. 2. Solid-state ^{13}C NMR data under different tillage systems: (A) aliphatic-C (0–108 ppm); (B) carbohydrate-C (60–96 ppm); (C) aromatic-C (108–162 ppm); and (D) aromaticity (108–145 ppm)/(0–162 ppm).
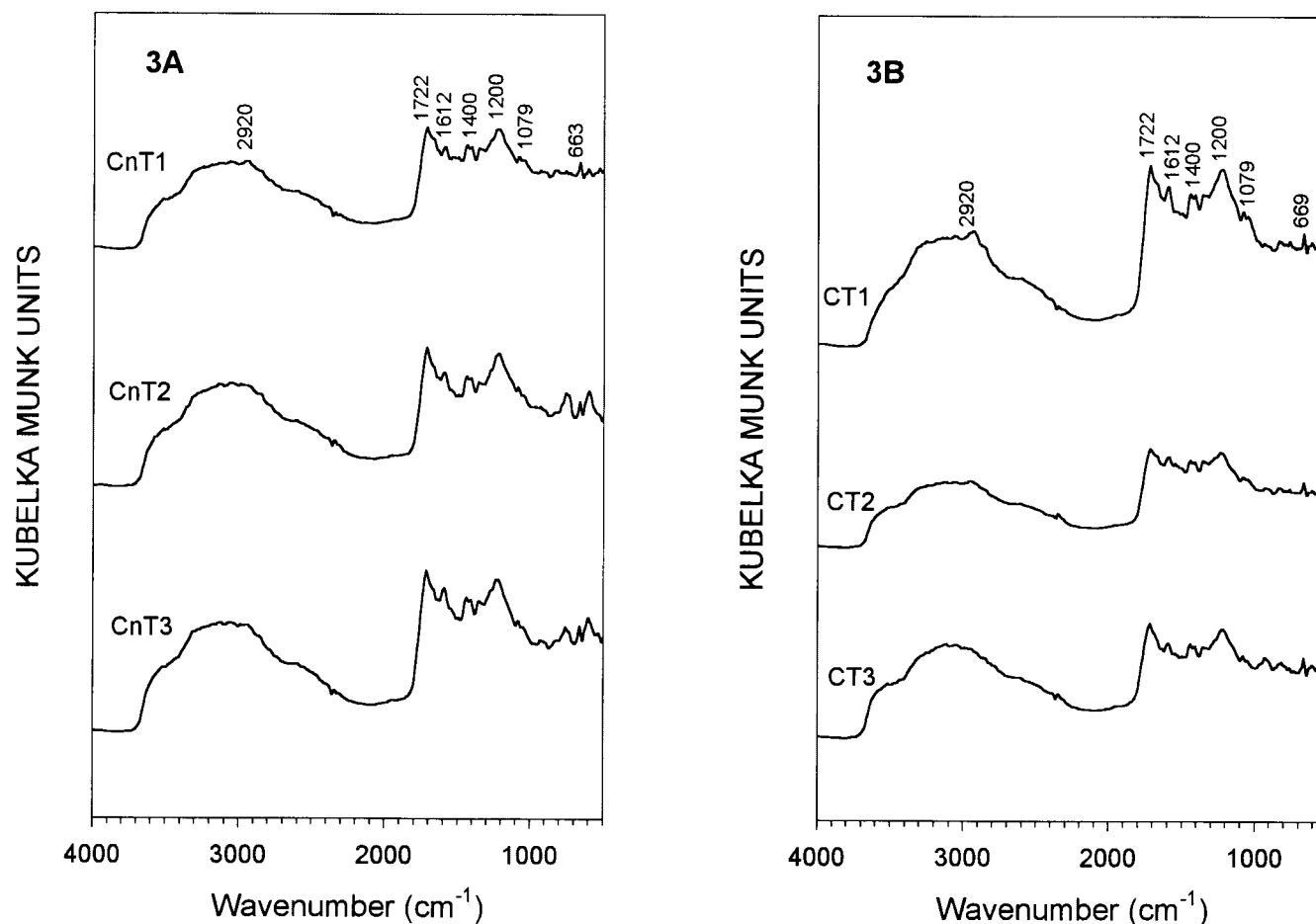
Fig. 3. Diffuse reflectance Fourier transform infrared spectra of humic acids in a Norfolk soil under different tillage treatments: (3A) conservation tillage treatment (CnT1, 0–5 cm; CnT2, 5–10 cm; and CnT3, 10–15 cm); (3B) conventional tillage treatment (CT1, 0–5 cm; CT2, 5–10 cm; and CT3, 10–15 cm).

and its content was very low (Fig. 1). We did not observe any distribution pattern and change between tillage treatments. This may be because of the poorly resolved carbonyl-C peaks (Fig. 1).

Diffuse Reflectance Fourier Transform Infrared Spectroscopy of Humic Acid

The spectra of HA from CT and CnT are presented in Fig. 3. The resolution of the spectra exhibited a significant improvement, compared with previously published spectra obtained using dispersive or FTIR spectrophotometers. Evidence for the presence of COOH groups was indicated by the peak at ~1200 cm^{-1}, which was attributed to C–O stretch and OH deformation of COOH groups. The band around 1620 to 1600 cm^{-1} in all of the HA spectra was assigned to aromatic C=C and the asymmetric C=O stretching in COO$^-$ groups (Inbar et al., 1989; Gressel et al., 1995). But the frequency at 1660 cm^{-1} can also be attributed to internal H bonds of carbonyl groups (Bellamy, 1975). Peaks ~1400 cm^{-1} were assigned to CH$_2$ and CH$_3$ bending, C–OH deformation of COOH, and COO$^-$ symmetric stretch (Celi et al., 1997). The bands in the 1100 to 900 cm^{-1} region were usually attributed to polysaccharide

and silicate vibrations (Francioso et al., 2000). The peak around 600 cm^{-1} of HA was associated with unknown mineral compounds (e.g., silicate, oxides, or organo-mineral fractions).

All DRIFT spectra of HA samples from CnT and CT systems were similar in their basic peak assignments. However, to get a clear picture of tillage impacts on spectral composition of HA, we examined ratios of reactive (O-containing) and recalcitrant (C, H, or N) functional group peak heights (Table 3). Based on peak ratio comparisons, the total O/R ratio (R_1) of HA was the highest at 0 to 5 cm of CnT system, which was significantly greater than that of CT system. The lowest O/R ratio appeared at the depth of 10 to 15 cm of CT treatment (Table 3). With increasing depth, the O/R ratio declined for both tillages (Table 3). There were relatively little changes of R_1 between 5- to 10- and 10- to 15-cm layers for both tillage systems. The ratio of ketonic and carboxyl (1727 cm^{-1}) groups divided by CH and aromatic peak heights (1457 + 1420 + 779 cm^{-1}) (R_2) was also the highest in the top soil (0–5 cm) of CnT system (Table 3), suggesting relatively enrichment of O associated C (e.g., carbohydrates) over time in CnT plots as compared with CT. However, there were

Table 3. Ratios of selected peak heights from DRIFT spectra of humic acids (Wander and Traina, 1996b).

HA	Depth	R_1 (O/R) $\dfrac{1727 + 1650 + 1160 + 1127 + 1050}{2950 + 2924 + 2850 + 1530 + 1509 + 1457 + 1420 + 779}$	R_2 $\dfrac{1727}{1457 + 1420 + 779}$
	cm		
CnT	0–5	0.87 (0.02)a†	0.51 (0.02)a
CnT	5–10	0.69 (0.01)b	0.44 (0.02)b
CnT	10–15	0.70 (0.01)b	0.43 (0.02)b
CT	0–5	0.74 (0.01)ab	0.44 (0.02)a
CT	5–10	0.69 (0.01)b	0.42 (0.01)a
CT	10–15	0.67 (0.01)b	0.43 (0.01)a

† Means with different letters are significantly different $P = 0.05$.

no significant differences of R_2 between soil depth for both tillages (Table 3).

DISCUSSION

Evaluating the effects of tillage on SOM dynamics has been shown to take almost 10 yr of experiment before any significant change (Hunt et al., 1996). It has been proposed that the LF be examined because it has been correlated with several procedurally defined soil fractions (e.g., biological pools). The LF may act as an indicator of organic matter status in soil (Wander and Traina, 1996a). Thus, characterizing the size of this fraction, as well as its C and N contents, may show short-term changes because of management practices, which may not be detected when measuring whole SOM pool.

In both tillages, the quantities of LF materials, LF-OC and LF-TCN were highly dependent on the SOC and soil-TCN contents. The CnT had higher yield of LF material in the top soil (0–5 cm) while CT soil had a higher amount of LF material in the 5- to 10-cm layer. The findings support the conclusions of Novak et al. (1996) that long-term CnT management creates a SOC-enriched surface zone. Conversely, SOC contents in the CT managements were fairly similar between soil layers probably as a result of mixing by disking. However, for assessing the effects of tillage and fallow frequency on soil quality, Campbell et al. (1999) reported that total organic C and N were surprisingly superior to the more labile attributes (e.g., microbial biomass). They had anticipated a significant influence of tillage on soil quality attributes, especially the labile ones, but they failed to obtain the expected results. This is probably because of the difference in soil texture and environmental conditions. They used a silty loam (Typic Haploboroll) in a cool-semiarid region (Saskatchewan, Canada), in comparison with a Norfolk loamy sand soil in a warm-humid region (South Carolina, USA) in our study.

Because HA is probably the largest single SOM pool in mineral soils, which is representative of the stage of humification, decomposition pathways have been studied most extensively using HAs (Guggenberger et al., 1994; Preston et al., 1994; Preston, 1996). In addition, without appropriate deashing treatments, low C contents and C/Fe ratios make humin extracted from soil mineral horizons to be a poor candidate for NMR analysis (Preston and Newman, 1995; Ding et al., 2001). Therefore, HA was used in this study. Soil samples were extracted three times for HA recovery in this work.

Even though there might be a small fraction of HA still left in soil, we believe that the HA samples would represent the overall characteristics of total HA.

Microbial decomposition of plant residue has a large influence on the elemental composition of SOM pool. In general, the compounds with narrow C/N ratios are in a more advanced stage of decomposition (Yakov-chenko et al., 1998). However, this was not the case for our HAs. The C/N ratio of HA ranged from 15.7 to 20.3 (for comparison, 10.4 to 13.5 for soil) (Tables 1 and 2) and increased with soil depth for both tillages. This result suggests that some N-containing compounds of SOM, particularly in the deeper soil layers, may be protected by physical encapsulation in three-dimensional structures with soil minerals, which were resistant to chemical extraction. Thus, N contents in the $Na_4P_2O_7$–extracted HA were relatively low (i.e., high C/N ratio). This finding was consistent with the reports of Knicker and Hatcher (1997), and Zang et al. (2000). By changing the conformational structure of HA, Zang et al. (2000) created new refractory organic N in HA. The newly formed proteinaceous materials in HA were physically encapsulated within the HA structure. They concluded that physical protection is one of the important factors accounting for the preservation of organic N in soils and sediments.

Examination of CPMAS-TOSS ^{13}C NMR data illustrated very interesting information. Compared with CT system, HA in the top soil (0–5 cm) of CnT had a higher proportion of carbohydrate-C (Fig. 2B). The trends observed were consistent with enhanced decomposition of plant inputs in the CT plot. This was supported by the relatively higher O/R ratio (R_1) of HA in the top (0–5 cm) soil under CnT management. The high O/R ratio indicated that SOM was more biological active. From this study, one may conclude that DRIFT and NMR can be used as complementary methods for the characterization of humic substances. This result also concurred with the LF data that CnT had a significantly higher LF material in the 0 to 5 cm of soil than that of CT plot, indicating that 20 yr of CnT management changed structures and compositions of SOM. Our results were in agreement with the observation that numbers of microbes, microbial biomass and potentially-mineralizable N were greater for no-tillage than CT in the 0- to 7.5-cm soil depth (Doran, 1980). These changes can be sufficient to differences in the available soil water content between tillages (Hunt et al., 1996).

Our observation of a substantial increase of aromatic-C in HAs with soil depth for both treatments implied that the humification processes were more advanced in deeper soil layers. This result was in good agreement with the report of Preston (1996) that as the aromatic rings of lignin are modified, a single broad peak with its maximum around 131 ppm starts to dominate in the aromatic region. With further humification, HAs may become highly aromatic, with development of polycondensed rings (Chen and Pawluk, 1995; Preston, 1996; Xing and Chen, 1999). Reduction of H/C ratio of HA in CnT plot (Table 2) with soil depth supported the increased aromaticity (Fig. 2D) as observed by NMR. However, this was not the case for the CT plot as H/C ratio was almost the same for all soil depths. The reason was unknown.

Although single composite sample was used for NMR analysis (because of the high cost and low availability of NMR instruments), the NMR results are consistent with the DRIFT and LF data where at least three replicates were used. Further, our NMR results are in agreement with that reported by other investigators for similar types of SOM research (Stearman et al., 1989; Preston et al., 1994; Francioso et al., 2000). Thus, the HA structural and compositional differences observed by NMR are most likely because of the tillage treatments.

From the data of LF, NMR, and DRIFT results of HA, the SOM in the top soil layer (0–5 cm) of CT plots seems more chemically and physically stable than CnT. This is consistent with the results of Stearman et al. (1989), Wander et al. (1994), and Wander and Traina (1996) that the CT soil had a greater proportion of all SOM in the more stable fraction. From a more practical point of view, CnT managements cannot only maintain the levels of SOC, but also substantially improve soil quality as reflected by reactive HA and high content of LF materials.

From the discussion above, it is clear that the tillage treatments have changed the chemical composition and structure of SOM. This can potentially affect pesticide fate and efficacy in soil. Nanny and Maza (2001) reported that the HA aromaticity and the solution pH influenced noncovalent interactions between HA and monoaromatic compounds. Celis et al. (1997) also reported that sorption of atrazine and simazine was higher on Fluka HA than on soil HA, even though the organic C contents of the two HAs were nearly the same. Moreover, sorption of organic compounds was positively correlated with aromaticity and negatively with polarity of SOM (Xing et al., 1994a,b,c; Xing, 1997; Ahmad et al., 2001). Sorption of several pesticides by the soils from both CnT and CT plots is currently under investigation.

CONCLUSIONS

Examinations of characteristics of LF material of a Norfolk soil under long-term CnT and CT management indicated that tillage can influence the distribution of LF in soil profile. The CnT treatment favored the build-up of surface plant residue which consequently increased the SOC and soil-TCN contents in the top soil

(0–5 cm). The CT treatment, on the other hand, mixed residue within the 15-cm soil layer. As a result, SOC and LF contents were higher at the deeper layers (5–15 cm) than CnT. The elemental composition of HA from two tillage systems was similar, but one cannot rely on elemental composition only in evaluating management effect. Though single composite samples were used, the solid-state ^{13}C NMR results showed that the aliphatic-C content of HA was higher in the top soil (0–5 cm) under CnT than CT. Conversely, the aromatic C of HA was higher in the top soil (0–5 cm) under CT than CnT. Aliphatic C of HA declined with the increase of soil depth under both tillages, whereas the aromatic C of HA increased with soil depth. For DRIFT analysis, although the spectra of HA were similar in their basic peak assignment, HA O/R ratio from the top soil (0–5 cm) of CnT treatment was higher than that from CT treatment, indicating that HA contained more recalcitrant functional groups in CT tillage. In sum, tillage management can substantially change the quantity and quality of SOM as reflected by relatively high contents of LF materials and more biologically active SOM in soils under CnT. Structural changes of SOM may change the sorptive behavior of pesticides in soils and their fates, efficiency, and uses. Future research has to address the relationship between spectroscopic characteristics and their agricultural significance.

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